10/588263
IAP11 Rec'd PCT/PTO 03 AUG 2006

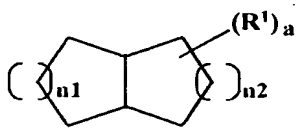
CLAIMS

Amendment of the Claim under Article 19(1) (Rule 46)

1. An immersion exposure liquid used for an immersion exposure device or an immersion exposure method in which a substrate is exposed through a liquid provided between a lens of a projection optical system and the substrate, the immersion exposure liquid being liquid in an operating temperature range of the immersion exposure device and comprising an alicyclic hydrocarbon compound or a cyclic hydrocarbon compound containing a silicon atom in its ring structure,

wherein the alicyclic hydrocarbon compound or the cyclic hydrocarbon compound containing a silicon atom in its ring structure has a transmittance of radiation with a wavelength of 193 nm of 70% or more at an optical path length of 1 mm and has a refractive index for D lines of 1.4 or more.

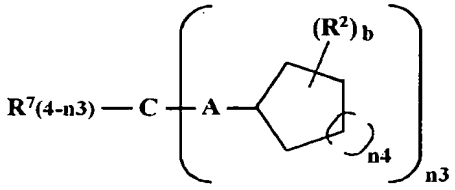
2. The immersion exposure liquid according to claim 1, wherein the alicyclic hydrocarbon compound or the cyclic hydrocarbon compound containing a silicon atom in its ring structure is at least one compound selected from compounds of the following formulas (1-1) to (1-9),



(1-1)

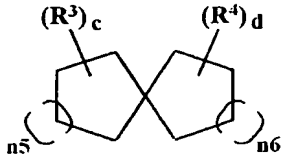
wherein R^1 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, n1 and n2 individually represent integers from 1 to 3, a represents an integer from 0 to 10, and provided that, when two or more R^1s exist, the R^1s may be the same or different, and

two or more R^1s may be bonded to form a ring structure,



(1-2)

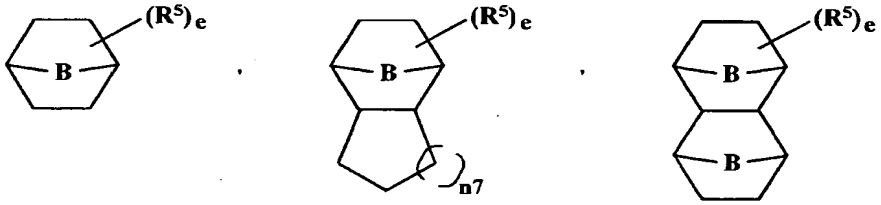
wherein A represents a single bond, a methylene group which may be replaced with an alkyl group having 1 to 10 carbon atoms, or an alkylene group having 2 to 14 carbon atoms which may be replaced with an alkyl group having 1 to 10 carbon atoms, R^2 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, R^7 represents a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a fluorine atom, or a fluorine-substituted alkyl group having 1 to 3 carbon atoms, provided that, when two or more R^7s exist, the R^7s may be the same or different, and two or more R^7s may be bonded to form a ring structure, n3 represents an integer from 2 to 4, n4 represents an integer from 1 to 3, b represents an integer from 0 to 6, and provided that, when two or more R^2s exist, the R^2s may be the same or different, and two or more R^2s may be bonded to form a ring structure,



(1-3)

wherein R^3 and R^4 represent an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or

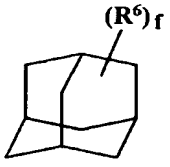
a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, provided that, when two or more R^3s and R^4s exist, the R^3s and the R^4s may be respectively the same or different, and two or more R^3s and R^4s may respectively form ring structures or may be bonded to form a ring structure, n5 and n6 represent integers from 1 to 3, and c and d represent integers from 0 to 8,



(a) (b) (c)

(1-4)

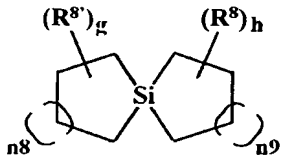
wherein B represents a methylene group or an ethylene group, R^5 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, e represents an integer from 0 to 10, n7 represents an integer from 1 to 3, and provided that, when two or more R^5s exist, the R^5s may be the same or different, and two or more R^5s may be bonded to form a ring structure,



(1-5)

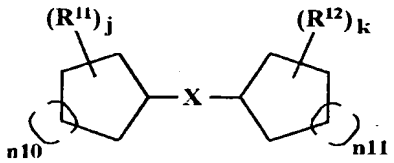
wherein R^6 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, f represents an integer from 0 to 10, and provided that, when two or more R^6s exist, the R^6s may be the

same or different,



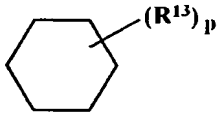
(1-6)

wherein R^8 and $R^{8'}$ represent an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, g and h individually represent integers from 0 to 6, and n8 and n9 represent integers from 1 to 3,



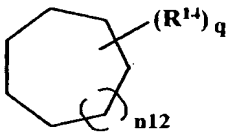
(1-7)

wherein R^{11} and R^{12} represent an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, n10 and n11 individually represent integers from 1 to 3, j and k represent integers from 0 to 6, provided that, when two or more R^{11}s and R^{12}s exist, the R^{11}s and the R^{12}s may be the same or different, and two or more R^{11}s may be bonded to form a ring structure or two or more R^{12}s may be bonded to form a ring structure, and X represents a single bond, a divalent aliphatic hydrocarbon group having 2 to 10 carbon atoms, or a divalent alicyclic hydrocarbon group having 3 to 14 carbon atoms,



(1-8)

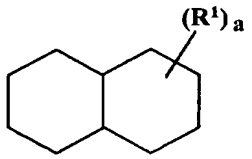
wherein R^{13} represents an alkyl group having two or more carbon atoms, an alicyclic hydrocarbon group having three or more carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 2 to 3 carbon atoms, p represents an integer from 1 to 6, and provided that, when two or more R^{13}s exist, the R^{13}s may be the same or different, and two or more R^{13}s may be bonded to form a ring structure,



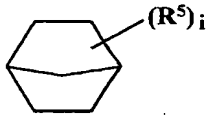
(1-9)

wherein R^{14} represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, n12 represents an integer from 1 to 3, q represents an integer from 0 to 9, and provided that, when two or more R^{14}s exist, the R^{14}s may be the same or different.

3. The immersion exposure liquid according to claim 2, wherein the compound of the formula (1-1) is shown by the following formula (2-1), and the compound of the formula (1-4) is shown by the following formula (2-2),



(2-1)



(2-2)

wherein, in the formula (2-1), R^1 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, a represents an integer from 0 to 10, and provided that, when two or more R^1s exist, the R^1s may be the same or different, and two or more R^1s may be bonded to form a ring structure, and, in the formula (2-2), R^5 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, i represents an integer from 0 to 2, and provided that, when two or more R^5s exist, the R^5s may be the same or different, and two or more R^5s may be bonded to form a ring structure.

4. The immersion exposure liquid according to claim 1, wherein, when contacting the liquid with a photoresist film for 180 seconds in a nitrogen atmosphere so that the liquid film has a thickness of 1 mm, the liquid shows a change in absorbance of light with a wavelength of 193 nm of 0.05 or less before and after the contact at an optical path length of 1 cm.

5. The immersion exposure liquid according to claim 1, wherein the immersion exposure liquid contains the alicyclic hydrocarbon compound or the cyclic hydrocarbon compound containing a silicon atom in its ring structure in an amount of 95 wt% or more of the immersion exposure liquid.

6. The immersion exposure liquid according to claim 1, wherein the immersion exposure liquid has a dissolved oxygen content of 2 ppm or less.

7. The immersion exposure liquid according to claim 1, wherein the immersion

exposure liquid has a total metal content of 10 ppb or less.

8. The immersion exposure liquid according to claim 7, wherein the metal is at least one metal selected from lithium, sodium, potassium, magnesium, copper, calcium, aluminum, iron, zinc, and nickel.

9. The immersion exposure liquid according to claim 1, wherein the immersion exposure liquid has a viscosity of 0.01 Pa·s or less at 25°C.

10. The immersion exposure liquid according to claim 1, wherein the immersion exposure liquid has a refractive index of 1.63 or more at a wavelength of 193 nm.

11. The immersion exposure liquid according to claim 10, wherein the immersion exposure liquid has a transmittance of radiation with a wavelength of 193 nm of 95% or more at an optical path length of 1 mm.

12. The immersion exposure liquid according to claim 3, wherein the compound of the formula (2-1) is trans-decahydronaphthalene, and the immersion exposure liquid has a transmittance of radiation with a wavelength of 193 nm of 95% or more at an optical path length of 1 mm and a dissolved oxygen content of 2 ppm or less.

13. The immersion exposure liquid according to claim 12, wherein the immersion exposure liquid is a liquid with a purity of 95 wt% or more which is obtained by subjecting a trans-decahydronaphthalene raw material to washing with concentrated sulfuric acid and distillation in a nitrogen atmosphere.

14. The immersion exposure liquid according to claim 3, wherein the compound of

the formula (2-2) is exo-tetrahydrodicyclopentadiene, and the immersion exposure liquid has a transmittance of radiation with a wavelength of 193 nm of 95% or more at an optical path length of 1 mm and a dissolved oxygen content of 2 ppm or less.

15. The immersion exposure liquid according to claim 14, wherein the immersion exposure liquid is a liquid with a purity of 95 wt% or more which is obtained by subjecting an exo-tetrahydrodicyclopentadiene raw material to washing with concentrated sulfuric acid and distillation in a nitrogen atmosphere.

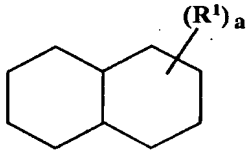
16. A method of producing the immersion exposure liquid according to claim 1, the method comprising subjecting the liquid comprising the alicyclic hydrocarbon compound or the cyclic hydrocarbon compound containing a silicon atom in the ring structure to at least one of washing with concentrated sulfuric acid and distillation in a nitrogen atmosphere.

17. An immersion exposure method comprising applying an exposure beam to a mask and exposing a substrate using the exposure beam through a liquid provided between a lens of a projection optical system and the substrate, the liquid being the immersion exposure liquid according to claim 1.

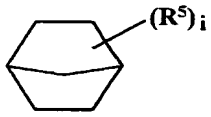
18. The immersion exposure method according to claim 17, wherein an immersion upper layer film is formed on a surface of a resist film on the substrate, the immersion upper layer film containing a resin component which is soluble in an alkaline developer and insoluble in the immersion exposure liquid according to claim 1 and containing at least one of a hexafluorocarbinol group and a carboxyl group as a substituent for providing the alkali solubility.

19. A method of evaluating the degree of contamination of an immersion exposure liquid during immersion exposure, the immersion exposure liquid being used for an immersion exposure device or an immersion exposure method in which a substrate is exposed through a liquid provided between a lens of a projection optical system and the substrate, the method comprising contacting the immersion exposure liquid with a photoresist film formed on the substrate in a nitrogen atmosphere, and comparing absorbances of the liquid measured for light with a wavelength of 193 nm before and after the contact to evaluate the degree of contamination of the immersion exposure liquid.

20. A liquid composition comprising a compound of the following formula (2-1) or (2-2) in an amount of 95 wt% or more and having a dissolved oxygen content of 2 ppm or less,



(2-1)



(2-2)

wherein, in the formula (2-1), R^1 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, a represents an integer from 0 to 10, provided that, and when two or more R^1s exist, the R^1s may be the same or different, and two or more R^1s may be bonded to form a ring structure, and in the formula (2-2), R^5 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a fluorine atom, or a fluorine-substituted hydrocarbon group having 1 to 3 carbon atoms, i represents an integer from 0 to 2, and provided that, when two or more R^5s exist, the

R^5s may be the same or different, and two or more R^5s may be bonded to form a ring structure.

21. The liquid composition according to claim 20, wherein the liquid composition has a total metal content of 10 ppb or less.

22. The liquid composition according to claim 20, wherein the compound of the formula (2-1) is trans-decahydronaphthalene, and the liquid composition has a transmittance of radiation with a wavelength of 193 nm of 95% or more at an optical path length of 1 mm.

23. The liquid composition according to claim 20, wherein the compound of the formula (2-2) is exo-tetrahydrodicyclopentadiene, and the liquid composition has a transmittance of radiation with a wavelength of 193 nm of 95% or more at an optical path length of 1 mm.

24. The liquid composition according to claim 20, wherein the compound of the formula (2-1) or (2-2) is purified by at least one of washing with concentrated sulfuric acid and distillation in a nitrogen atmosphere.

Explaining the Amendment under Article 19 (1)

Amended Claim 1 discloses that a liquid according to the present invention is used for an immersion exposure such as ArF excimer laser. JP-A-9-241214 discloses an immersion oil useful for preparing a microscope, and the immersion oil is oily material. JP-A-7-220990 does not disclose a specific immersion exposure liquid. JP-A-2001-326162 discloses a technology related to an oxygen elimination, but does not disclose an oxygen elimination in liquids. WO 1999/049504 A1 is an example of use of pure water as an immersion medium, and the contained impurities are different from that of present invention. WO 2003/016365 A1 and WO 2001/032739A do not disclose any immersion exposure liquids.